

may be deposited within the ligand "cavity" closer to the electrode, thus lowering the energy barrier for further electron transfer. Voltammetrically, the initial barrier is manifested as an increased overpotential for the reduction, i.e. a negative shift of the reduction potential, whereas the easier electron transfer provided by the first layer of deposited Cu atoms gives rise to an autocatalytic effect, appearing as an enhanced reduction current (and thus a loop) of the reverse scan. Experiments with decreasing reversal potentials (not shown) indicate that even submonolayer amounts of Cu atoms may cause such appreciable catalytic effects.

From the negative shift of the  $\text{Cu}^{2+}$  reduction peak potential, observed with Au/(TBEA + OM) relative to a bare gold electrode (FIGS. 2g and i), and considering a tunnelling mechanism for the electron exchange with the metal, one can estimate the potential shifts to be expected for varying distances between  $\text{Cu}^{2+}$  and the underlying electrode. To verify these expectations, a new ligand molecule which contains an additional methylene group, 3,3'-thiobispropyl acetoacetate,  $\text{S}(\text{CH}_2\text{CH}_2\text{CH}_2\text{OCOCH}_3)_2$  (TBPA), was prepared and tested under identical electrochemical conditions. Assuming a similar orientation of the two ligands with respect to the substrate, the metal ion with TBPA should be located 0.5–1.0 Å further away from the gold surface than with TBEA. Indeed, this results in a reduction peak potential more negative by ~0.030 V for the deposition of Cu with TBPA (FIG. 2g and h), which agrees qualitatively with the proposed tunnelling mechanism.

#### EXAMPLE 2

Under certain conditions one single compound can fulfil both functions, selectivity and blocking. Sputter deposited gold on a glass slide was annealed for 3 h at 250° C. and thus there was produced a gold layer which was smoother by a factor of 2–3 compared with untreated sputter-deposited gold. A TBEA monolayer was absorbed according to the usual procedure and a layer of considerably better quality was obtained. No additional blocking agent was required. When the Au/TBEA was tested electrochemically in the same manner, in a 0.1 M  $\text{H}_2\text{SO}_4$  containing 1.0 mM  $\text{Cu}^{2+}$  and 3.0 mM  $\text{Fe}^{3+}$ , it displayed the same selectivity as was achieved with mixed monolayers of the other examples on a regular gold substrate.

#### EXAMPLE 3

Selective behaviour is observed when TBEA is replaced with TBPA or when the blocking agent OM is replaced with naphthol polymer (NP) or polymerizable octadecyl trichlorosilane (OTS). Diffusion-controlled faradaic currents are generally enhanced at randomly distributed pinholes. A situation in which the bulk-copper peaks are prominent whereas copper "under potential" and  $\text{Fe}^{3+}/\text{Fe}^{2+}$  peaks are totally absent would therefore require rather unusual size and spatial distributions of pinholes. Being deposited electrochemically, NP should block all uncoated electrochemically accessible sites. An NP layer of comparable thickness on a bare gold surface indeed blocks copper deposition completely. Ionic competition experiments provide strong experimental support for the selective complexation model.  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  ions, which resemble  $\text{Cu}^{2+}$  at coordination requirements, successfully replace  $\text{Cu}^{2+}$  at monolayer ligand sites although being electrochemically inactive under the present conditions. The  $\text{Cu}^{2+}$

peaks are suppressed in the presence of  $\text{Zn}^{2+}$ , and at a high  $\text{Zn}^{2+}$  concentration (~8.0 mM) the  $\text{Cu}^{2+}$  peaks cannot be detected at all. The same is observed with  $\text{Cd}^{2+}$  (in both cases the peaks are fully recovered in pure  $\text{Cu}^{2+}$  solution). Conversely, the presence of non-complexing ions, such as  $\text{Fe}^{3+}$  or  $\text{Ce}^{3+}$ , has essentially no effect on copper deposition. The complete disappearance of  $\text{Cu}^{2+}$  peaks in these competition experiments indicates the absence of electrochemically active pinholes down to <0.005% of the total area.

#### LEGENDS TO FIGURES

FIG. 1 is a schematic representation of TBEA,  $\text{Cu}^{2+}$ -TBEA complex, and n-octadecyl mercaptan (OM), adsorbed on gold substrate. Note that the ligand binds  $\text{Cu}^{2+}$  in the enol form upon losing two protons, and thus the complex is neutral. TBEA was prepared by the 4-dimethylaminopyridine (DMAP)-catalysed reaction of 2,2'-thiobisethanol with diketene. Gold electrodes were prepared by sputter-deposition of ~1,000 Å gold on glass microscope slides followed by annealing for 15 min at 420° C., which reduces the gold-surface roughness.

FIG. 2 presents cyclic voltammograms in 0.1 M  $\text{H}_2\text{SO}_4$  containing 1.0 mM  $\text{Cu}^{2+}$ , 3.0 mM  $\text{Fe}^{3+}$ , or both (scan rate: 0.10 V s<sup>-1</sup>; electrode area: 0.63 cm<sup>2</sup>; MSE is mercurous sulphate reference electrode, +0.400 V versus saturated calomel electrode). a, Au in  $\text{Cu}^{2+} + \text{Fe}^{3+}$ ; b, Au/TBEA (~80% coverage) in  $\text{Fe}^{3+}$ ; c, Au/(-TBEA + NP) in  $\text{Fe}^{3+}$ ; d, Au/TBEA + OM in  $\text{Fe}^{3+}$ ; e, Au/(-TBEA + NP) in  $\text{Cu}^{2+}$ ; f, Au/(-TBEA + NP) in  $\text{Cu}^{2+} + \text{Fe}^{3+}$ ; g, Au/(TBEA + OM) in  $\text{Cu}^{2+} + \text{Fe}^{3+}$ ; h, Au/(TBPA + OM) in  $\text{Cu}^{2+} + \text{Fe}^{3+}$ ; i, Au in 0.1 M  $\text{H}_2\text{SO}_4$  containing 0.4 M ethyl acetoacetate and either  $\text{Cu}^{2+}$  (solid line) or  $\text{Fe}^{3+}$  (broken line). The ligand coverage was estimated from the minimal amount of charge required to block Au/(-TBEA) with naphthol polymer (towards  $\text{Fe}^{3+}$ ) compared to that required to block a bare electrode of the same geometric area. Surface coverages of ca. 80% with TBEA are typical. Essentially the same curves as c and d are obtained, respectively, for Au/NP and Au/OM in either  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ , or  $\text{Cu}^{2+} + \text{Fe}^{3+}$ . For c,e,f, naphthol polymer (NP) was deposited in a stirred solution containing 1.0 mM 1-naphthol in 0.5 M  $\text{H}_2\text{SO}_4$  by passing a constant anodic current of 2.0  $\mu\text{A cm}^{-2}$  for 4.5 min. This corresponds to about 10 layers of NP deposited at ligand-uncovered sites of the electrode, which results in a NP film thickness comparable with that of the ligand monolayer itself.

FIG. 3 illustrates RA-FTIR spectra of: a,  $\text{Cu}^{2+}$ -TBEA complex in a Au/( $\text{Cu}^{2+}$ -TBEA + OM) electrode (specimen obtained by immersion of Au/(TBEA + OM) in saturated aqueous copper acetate solution adjusted to pH 7.5 with sodium acetate, for 1.5 h at 40–45° C.); b, TBEA in the electrode of a, after electrochemical removal of the  $\text{Cu}^{2+}$  by cycling three times in 0.1 M  $\text{H}_2\text{SO}_4$  between +0.35 V and -0.75 V (v. MSE); c, TBEA in bulk liquid. The spectra in a and b were produced by a weighted subtraction of Au/OM spectrum from the spectra of the respective electrodes in a and b. The spectral features in the 3,000–2,800 cm<sup>-1</sup> region represent various C-H stretch modes. The peaks at 1,744 and 1,716 cm<sup>-1</sup> are C=O stretch modes of the ester and ketone functions, respectively, of TBEA in the keto form. The features between 1,660 and 1,510 cm<sup>-1</sup> are characteristic of the  $\text{Cu}^{2+}$ -acetoacetate complex, the bands around 1,660 cm<sup>-1</sup> (a,b) and 1,653–1,630